INVESTIGATION OF THE CHANGES OF THE ROTATION-VIBRATION SPECTRUM OF CERTAIN SIMPLE MOLECULES DURING DISSOLUTION

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ABSTRACT. Additional absorption bands unassociated with the intramolecular degrees of freedom have been detected in the infrared spectra of the solutions of hydrogen halides in water. By comparing the spectra of solutions with the spectra of gases the additional bands were interpreted as the diffuse groups of rotational branches. This indicates that the almost free rotation of dissolved substance molecules is retained in solutions. As the interaction with the solvent increases rotation changes to libration.

The transition of a material from the vapor state into a liquid state or /569* into a solution is accompanied by the disappearance of the rotational band structure in the vibrational spectrum. It is usually assumed that this phenomenon is associated with the impossibility of free molecular rotation in liquids.

The minimum perturbation of rotational movement takes place in liquid hydrogen where a discrete rotational spectrum is observed (ref. 1). In the case of liquid oxygen, nitrogen and methane discreteness is no longer present (ref. 2) and only the form of the bands in the Raman scattering spectra indicates that the almost free rotation of their molecules is retained.

Repeated efforts have been made to detect the rotation of molecules in solutions. It is natural to conduct such experiments initially with light molecules which have small moments of inertia and large rotational quanta.

With this purpose in mind Kinsey and Ellis (ref. 3) investigated the infrared absorption spectra of water dissolved in CCl_4 and CS_2. They associated the established structure of the 1.38 and 1.87 μ bands with the quantized rotation of the H_2O molecule. Similar results were obtained by Borst, Buswell and Rodebush (ref. 4) for the 2.7 μ band of H_2O. However, their data were not confirmed by the rather meticulous work of Fox and Martin (ref. 5), who showed that the structure is explained by the noncompensated absorption of atmospheric water vapors. Fox and Martin discovered an additional absorption band on the slope of the ν_3 band for water dissolved in CCl_4. In their opinion the form of the additional band resembles the envelope of rotational lines in the spectrum of water vapor. The existence of this band is also noted in the works of Chulanovskiy (ref. 6) and of Mecke and co-workers (ref. 7).

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Numbers in the margin indicate the original pagination in the foreign text.

A series of works (refs. 8-10) studied the absorption spectrum of methane dissolved in CCl_4. According to Breneman and Williams (ref. 9) the rotational structure of the $\nu_3 CH_4$ band is observed. However, this is disproved by the data of Fox and Martin (ref. 8) and of Paillard (ref. 10).

West and Edwards (ref. 11) who investigated the infrared spectra of hydrogen chloride solutions detected 2 secondary maxima is smaller intensity in the CCl_4 solution, on both sides of the central absorption maximum, for the basic HCl tone. Similar band forms were observed by Buswell, Maycock, Rodebush, (ref. 12) for the solution of HF in CCl_4 while Josien and Sourisseau (ref. 13) observed it for solutions of HCl and HBr in CCl_4 and CS_2. These auxiliary maxima were interpreted as combinations of the intramolecular frequency with the intermolecular oscillations frequency of the HHal molecules bound with the solvent (ref. 11).

Thus it appears that, to date, the rotational structure in the spectra of solutions has not been observed with reliability. At the same time additional bands have been observed in a series of cases but the origin of such bands was not subjected to a special investigiation.

The present work investigates the infrared absorption spectra for solutions of hydrogen halides in water for the purpose of investigating the question of association between the form of the band and the nature of molecular motion in liquid media as well as for the clarification of additional bands in the spectra of solutions. /570

Experimental Part

The measurements were carried out by means of the IKS-6 and Perkin-Elmer (Model 12-B) spectrometers with LiF and NaCl prisms. The instruments were calibrated by using the absorption spectra of gaseous H_2O, CO, HBr, HCl and NH_3. The error in determining the frequency was ± 2 cm^{-1} for narrow bands and approximately ± 5 cm^{-1} for wider bands.

The utilized solvents were purified by the usual chemical methods and by multiple distillation. The degree of purity was controlled by the boiling point, by the index of refraction, and spectroscopically. Diluted solutions were investigated; the thickness of the layers d was 0.05-8.0 cm. At elevated temperatures the spectra were read with the aid of a vessel heated by a water jacket connected to a precision thermostat.
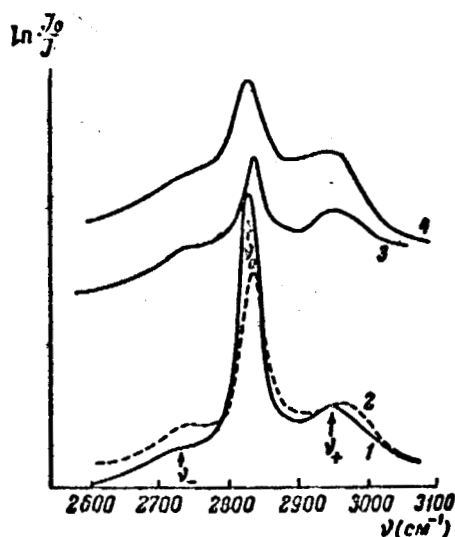
Figure 1. The infrared absorption spectra for solutions of hydrogen chloride.

$S=5$ cm^{-1} at 2700 cm^{-1}; (d=1 cm).
Solvent: 1-CCl$_4$, t=19°, 2-CCl$_4$,

t=95°, 3-TiCl$_4$ (d=2 cm), 4-SiCl$_4$.
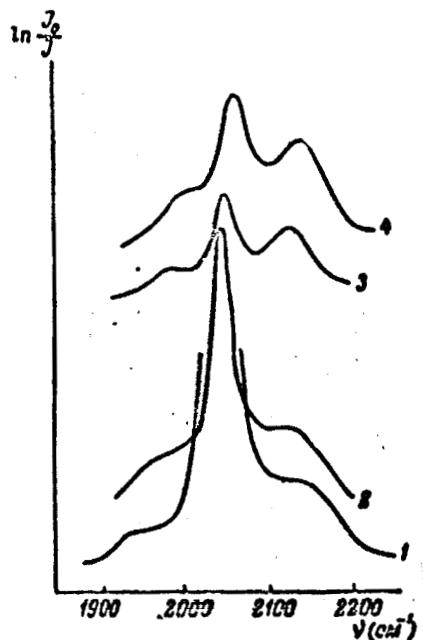
Figure 2. The infrared absorption spectra of deuterium chloride solutions.

$S=2$ cm^{-1} at 2000 cm^{-1}, d=1 cm.
Solution: 1-CHCl$_3$; 2-CCl$_4$,

3-TiCl$_4$, 4-SiCl$_4$.

Spectra were obtained for solutions of HCl in CCl$_4$, SiCl$_4$, TiCl$_4$, DCl and CCl$_4$, SiCl$_4$, TiCl$_4$, CHCl$_3$; HBr and DBr in CCl$_4$; HF in C$_5$F$_{12}$; H$_2$O in C$_3$Cl$_2$F$_6$, C$_2$Cl$_3$F$_3$, CCl$_4$, C$_2$Cl$_4$, CHCl$_3$CH$_3$NO$_2$ and D$_2$O in C$_2$Cl$_3$F$_2$ at room temperature (approximately 19°), and also for HCl and HBr in CCl$_4$ at 95°, H$_2$O in CCl$_4$ at 75° and in CH$_3$NO$_2$ at 90°. Part of the obtained spectra is represented in figures 1-5 (the captions for the figures present the values of S--the effective spectral width of the slit).

As we can see from figs. 1, 2 and 3 the bands of all the hydrogen halides in solutions consists of a central absorption peak and of auxiliary maxima situated on both sides of it. The positions of the central band and of the high frequency and low frequency side maxima are designated respectively by ν_0, ν_- and ν_+ and shown in table 1. In the case of gases these designations refer

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to the frequencies of the zero band and to the maxima of the P and R branches. By comparing figs. 1 and 2 we can see that the distance between the side maxima $\Delta\nu=\nu_{+}-\nu_{-}$ differs little for various solvents and decreases noticeably when we go from HHal to DHal.

The intensity of these maxima with respect to the central band increases when the following sequence of solvents is used: $CHCl_3$, CCl_4, $TiCl_4$, $SiCl_4$, C_5F_{12}. For the spectrum of hydrogen fluoride in C_5F_{12} (fig. 3) the side bands have approximately the same intensity as the central band. Absorption on the side of lower frequencies belongs to the associated HF molecules.

TABLE 1.   VARIATION IN THE ROTATIONAL-VIBRATIONAL SPECTRUM DURING SOLUTION.

Hydrogen halide	Solvent	ν_0 (cm^{-1})	ν_+ (cm^{-})	ν_- (cm^{-1})	$\Delta\nu$ (cm^{-1})	$\Delta\nu_{HHal}/\Delta\nu_{DHal}$
HCl	gas	2886 [14]	2973	2827	146	} 1.51
DCl	gas	2091 [15]	2147	2050	97	
HCl	} CCl$_4$	2327	2945	2730	215	} 1.43 ± 0.16
DCl		2043	2125	1975	150	
HCl	} TiCl$_4$	2828	2940	2750	190	} 1.45 ± 0.19
DCl		2046	2121	1990	131	
HCl	} SiCl$_4$	2835	2950	2742	205	} 1.47 ± 0.18
DCl		2049	2129	1990	139	
DCl	CHCl$_3$	2046	2145	1960	185	—
HBr	gas	2558 [16]	2629	2510	119	} 1.55
DBr	gas	1839 [17]	1882	1805	77	
HBr	} CCl$_4$	2515	2620	2440	180	} 1.48 ± 0.18
DBr		1814	1890	1765	125	
HF	gas	3962 [18]	4090	3885	205	—
HF	C$_5$F$_{12}$	3936	4075	3825	250	—

Remark.   The data are for room temperature.
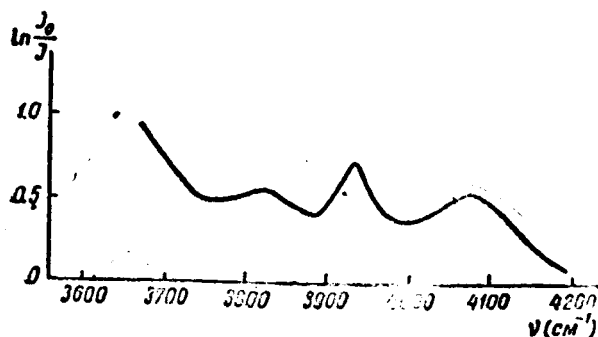

Figure 3.   The infrared absorption spectrum for the solution of hydrogen fluoride in C_5F_{12}.

$S=8$ cm^{-1} at 4000 cm^{-1}, $d=1$ cm.

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When the temperature is raised the central peaks for HCl and HBr in CCl$_4$ solutions are displaced toward the higher frequencies, there is an increase in splitting $\Delta\nu$, while the intensity of side maxima does not decrease in any case.

In the spectra of water solutions 2 bands are constantly observed. These correspond to the symmetric (ν_1) and antisymmetric (ν_3) valence oscillations of <u>/572</u> which the latter, as a rule, is more intense. Figure 4 shows the spectrum for the solution of D$_2$O in C$_2$Cl$_3$F$_3$. The 2766 and 2654 cm^{-1} bands refer to the ν_3 and ν_1 oscillations respectively. The band situated between them refers to the oscillation ν_1, of the HDO molecules which are formed by isotropic exchange with residues of light water in the solvent. On the side of higher frequencies a clear auxiliary absorption band (fig. 4, 2) is observed away from the ν_3 band.

Similar side maxima exist in the spectra of light water solutions (fig. 5). The form of the corresponding maximum in nitromethane differs noticeably from the others; while in all other solutions the centers of side maxima are removed from the peak of the valence band by 100-120 cm^{-1}, in the case of CH$_3$NO$_2$ this distance is approximately 250 cm^{-1}. The investigation of H$_2$O spectra in CCl$_4$ and CH$_3$NO$_2$ at elevated temperature shows that the behavior of additional maxima is different in these solutions. In nitromethane there is a noticeable displacement of the side maxima toward the lower frequencies (fig. 5 and 6) when the temperature is increased and decrease in the distance to the valence bands; in carbon tetrachloride such changes were not observed.
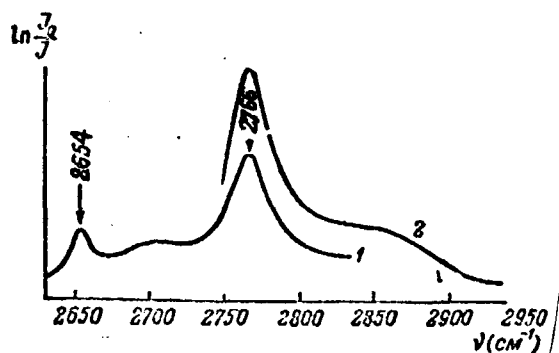

Figure 4. The infrared absorption spectrum for the solution of heavy water in C$_2$Cl$_3$F$_3$:

S=10 cm^{-1} at 2700 cm^{-1}. Layer thickness (in cm): 1-5; 2-8.
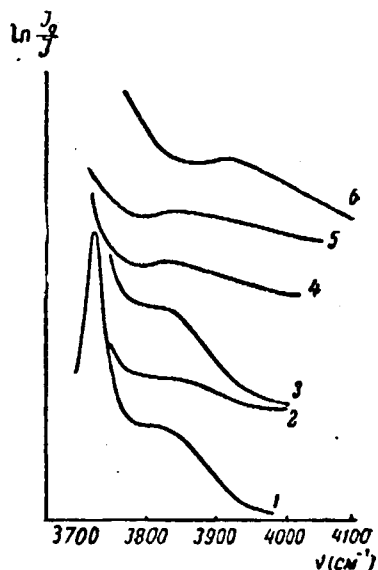
Figure 5. The infrared absorption spectra of water solutions.

$S=10$ cm^{-1} at 4000 cm^{-1}. Solvent: $1-C_2Cl_3F_3$, $d=10$ cm, $2-C_3Cl_2F_6$, $d=5$ cm, $3-CCl_4$, $d=5$ cm, $t=19°$, $4-CHCl_3$, $d=0.5$ cm, $5-CH_3NO_2$, $d=1$ cm, $t=90°$, $6-CH_2NO_2$, $d=1$ cm, $t=19°$.

TABLE 2.

Solvent	In kilocalories/ mole	In cm^3/mole
$CHCl_3$ . . .	7.97 [23]	6.4
CCl_4 . . .	7.97 [23]	7.7
$TiCl_4$ . . .	8.96 [24]	7.8
$SiCl_4$ . . .	~7.0 [23]	9.2
C_5F_{12} . . .	6.08 [25]	19.2

Remark: V_{free} was determined at a temperature of 20-25°.

Discussion of Results

Until the present time the nature of the described side absorption bands remained obscure. The simplicity of the molecules whose spectra were used to observe this type of band makes it possible for us to affirm that they are not associated with the intramolecular degrees of freedom. They cannot be attributed to "simultaneous transitions" (ref. 19). This is demonstrated, in particular, by changes which take place in the spectrum when HHal is replaced by DHal. It remains for us to admit that the appearance of these maxima is due to the motion of the dissolved substance molecules as a whole.

The data obtained in the present work agree, best of all, with the proposition that such motion in most cases is the poorly retarded rotation of molecules in the solution. In the first place our attention is drawn by the similarity between the forms of the bands in the spectra of hydrogen halide solutions and the envelope of the P, Q and R branches. We can see from the data of table 1 that the high frequency side maximum is at a greater distance from the central band than the low frequency side maximum. In the spectrum of the gas the maxima of the R and P branches are situated in a similar manner with respect to the zero maximum. Changes observed in the spectra of solutions during heating are similar to changes which take place in the spectrum of a gas: for diatomic molecules the relationship between splitting in the Bierrum doublet $\Delta\nu$ and the temperature T is given by the following equation

$$\Delta\nu_9 = 4B\sqrt{\frac{2kT}{Bhc}}$$

(B is the rotational constant), i.e., $\Delta\nu_9$ increases with temperature. A similar relationship is observed in the spectra of solutions. If the auxiliary maxima have the same nature as the P and R branches then the isotopic effect must be the same in both cases. Indeed the calculation of ratios $\Delta\nu_{HHal}/\Delta\nu_{DHal}$ for gases and solutions shows that they coincide within the limits of experimental error (see table 1). It is also interesting to note that the HCl band in the spectrum of the compressed gaseous mixture of HCl and N_2 at pressures of approximately 1000 atmospheres, investigated by Vodar (ref. 20) has a form which resembles the form of bands in solutions.

The auxiliary bands in the spectra of water solutions give all indications that their nature is the same as in hydrogen halide solutions. They are more diffused which is easy to understand if we note that water molecules are asymmetric gyroscopes whose rotational-vibrational spectrum is rather complex.

The case of nitromethane serves as an exception. The unusual temperature behavior of the side maximum in CH_3NO_2 resembles the behavior of the 2100 cm^{-1} band in the spectrum of liquid water. This band is attributed to the combination of the deformation oscillation ν_2 of H_2O with the intermolecular oscillations

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of the libration type, and is also displaced in the direction of lower frequencies during heating (ref. 5, 21). This fact as well as the abnormally large removal of the side maximum from the intramolecular band for H_2O makes us believe that in the CH_3NO_2 the motion of water molecules takes on oscillatory, libration nature.

This interpretation coincides with the interpretation proposed by West and Edwards, (ref. 11).

The perturbation of the rotational motion associated with the molecule of a dissolved substance is small as long as its potential energy V remains less than the kinetic energy (ref. 22). This situation exists in most of the solutions investigated by us. As the interaction with the solvent increases the potential energy will increase and when $V > kT$ the motion of the molecules is transformed into vibrational motion which is accompanied by an increase in the frequency of the transition which combines with the basic one as, for example, in the solution of water in nitromethane. The relatively high value of H_2O solubility also points to a stronger interaction of components in this system.

The problem of auxiliary maxima intensity has not been considered quantitatively in the present work because the determination of intensity was complicated by the strong overlap of these maxima with the bands of intramolecular oscillations. We only note that the increase in the intensity of side maxima with respect to the central maximum takes place in the spectra of hydrogen halides in parallel with the increase which is practicable for the movement of the free volume of solvents. The variation in the free volumes V_{free}, which are computed by means of the Lutskiy equation (ref. 26) can be seen in table 2 which also presents the heats of vaporization for the investigated solvents.

In conclusion the author expresses his deep gratitude to V. M. Chulanovskiy for supervising the work and discussing its results.

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